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(54) METHOD OF TREATING WASTEWATER LADEN WITH FINE CARBONACEOUS COAL AND INORGANIC PARTICLES

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TITLE

A METHOD OF TREATING WASTEWATER LADEN WITH FINE CARBONACEOUS COAL AND INORGANIC PARTICLES

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ABSTRACT OF THE DISCLOSURE

The problem of treating wastewater containing coal tailings with flocculants in a thickener to separate the water is overcome by first reducing the water of the wastewater, then micro-agglomerating carbonaceous coal particles and separating them from the remaining water and inorganic (clay) particles, and then using ultrafiltration to leave a viscous, thickened residue for disposal. The initial thickening may be replaced by a first, ultrafiltration step and the separated water is reusable.

This invention relates to a method of treating wastewater laden with fine carbonaceous coal and inorganic particles.

The treatment, recovery of coal from, and/or disposal of clay from wastewater laden with fine coal and clay, from coal preparation plants with attendant water reclamation is one of the most serious problems facing the coal preparation plant operator today. Furthermore, the use of mechanical mining equipment has resulted in an ever increasing amount of wastewater laden with fine coal and clay in run-of-mine coal. The problem of fine coal and clay generation and their retention in the water circuits of the plants can only increase as the demand for cleaner coal grows on the one hand, and the quality of mined coal deteriorates on the other. Finer grinding for release of impurities to "deep-clean" these coals is inevitable, together with the attendant wastewater laden with fine coal and clay generation problems.

On the water reclamation side, the need for water economy is growing as suitable feed water sources for preparation plants become more scarce. More stringent pollution regulations on the plant effluent have necessitated water recirculation with the attendant need for better processes to remove clay from and recover coal from the water circuit.

The conventional operation today is to thicken the fines reject in a thickener with the use of a flocculant to help clarify the recirculating water for reuse in the plant. The thickener underflow is then pumped to an impoundment area for later reclamation of water after settling and final dredging of the solids to be mixed with coarser refuse. Alternatively, the thickener underflow is filtered to recirculate the filtrate water and dispose of a filter cake of solids.

One problem that exists with the use of thickeners is that the presence of the carbonaceous particles of the fine coal requires an unduly large amount of flocculant to be used.

It has now been found, according to the present invention that coal agglomeration in combination with ultrafiltration provides a solution to these fine coal treatment problems in a number of ways.

According to the present invention there is provided a method of treating wastewater laden with fine coal and clay particles, comprising:

a) separating water from the particle laden wastewater to bring the particulate solids content thereof within the range of the order of 10 to of the order of 35 weight %, then,

b) mixing the particle laden wastewater with oil agglomerating liquid to micro-agglomerate fine, carbonaceous coal particles of the particle laden wastewater, the oil agglomerating liquid additive being added at not more than of the order of 20 weight % of the total weight of the solids of the particle laden wastewater,

c) separating the agglomerated fine, carbonaceous coal particles from the remainder of the particle laden wastewater to leave particulate, inorganic material laden wastewater, and then,

d) dewatering the particulate, inorganic material laden wastewater by ultrafiltration to leave a viscous, thickened particulate, inorganic material residue.

In some embodiments of the present invention the water is separated from the particle laden wastewater, to bring the particulate solids content within the range of the order of 10 to of the order of 35 weight %, by ultrafiltration.

In other embodiments of the present invention, the water is separated from the particle laden wastewater, to bring the particulate solids content within the range of the order of 10 to of the order of 35 weight %, by thickening the particle laden wastewater to clarify water thereof and then separating the clarified water therefrom.

In some embodiments of the present invention, water is separated from the particulate, inorganic material laden wastewater, from which the agglomerated carbonaceous particles have been removed by thickening the particulate, inorganic laden wastewater prior to the dewatering by ultrafiltration.

In some embodiments of the present invention, the dewatering of the particulate, inorganic material laden wastewater brings the particulate solids content to greater than of the order of 40 weight %.

In other embodiments of the present invention the water from the said thickening step is purified by ultrafiltration.

Preferably the ultrafiltration step is carried out using porous, polysulfone ultrafiltration membrane material.

Preferably the ultrafiltration step to separate water, to bring the particulate solids content within the range of the order of 10 to of the order of 35 weight %, is carried out using porous, polysulfone ultrafiltration membrane material.

By agglomerating the fine, carbonaceous coal particles to reduce the solids content of the wastewater from the order of 10 to of the order of 35 weight %, one problem of excess flocculant usage due to the presence of excessive carbonaceous coal particles is overcome.

Where the clarity of the thickener overflow is a problem, ultrafiltration at these low solids concentrations (usually less than 5% solids) in the wastewater produces clear recycle water at potentially economic flux rates. Wastewater containing less than 10-35% solids can be concentrated by ultrafiltration to produce a denser slurry which is suitable for the agglomeration step, thus further reducing the flocculant problem with the carbonaceous particles of the coal.

However, in some embodiments of the present invention, a thickener is used at shorter residence periods and higher capacities to accomplish the initial wastewater solids concentration, followed by agglomeration to remove the carbonaceous particles, and then ultrafiltration units to concentrate the inorganic material laden wastewater to a solids content range where thickeners are generally less efficient.

However, depending on the characteristics of the particulate, inorganic material present in the wastewater from the agglomeration, it may be desirable to use a thickener after the agglomeration step and before the final ultrafiltration step.

In the accompanying drawings which illustrate, by way of example, embodiments of the present invention:

Figure 1 is a flow sheet of a method of treating wastewater laden with fine coal particles and clay.

Figure 2 is a similar flow sheet to Figure 1 but of a different method of treating wastewater laden with fine coal particles and clay.

Figure 3 is a graph showing the effect of operating pressure on pure water permeation (PWP) rate through cellulose acetate membranes.

Figure 4 is a diagram of a test apparatus to verify the use of ultrafiltration membranes for separating coal particles and clay from water.

Figure 5 is a graph showing the effect of operating pressure and feed flow rate on water flux through cellulose acetate membranes using 2% coal-water feed slurry.

Figure 6 is a graph showing the effect of solids concentration in coal-water feed slurry on water flux through cellulose acetate membranes at an operating pressure of 276 kPag (40 psig) and feed flow rate of 34.1 m^3/min (90 gal/min) in each module.

Figure 7 is a graph showing the effect of solids concentration in clay-water feed slurry on water flux through cellulose acetate

membranes at an operating pressure of 276 kPag (40 psig) and feed flow rate of 34.1 m^3/min (90 gal/min) in each module.

Figure 8 is a graph showing the effect of solids concentration in coal-water feed slurry on water flux through polysulfone membranes at an operating pressure of 276 kPag (40 psig) and feed flow rate of 34.1 m^3/min (90 gal/min) in each module.

Figure 9 is a graph showing the processing capacities of cellulose acetate membranes in a module, and polysulfone membranes used for the concentration of solids in coal-water and clay-water slurries at the operating pressure of 276 kPag (40 psig) and feed flow rate of 34.1 m^3/min (90 gal/min) in each module.

Referring now to Figure 1, there is shown a method of treating wastewater from a coal preparation plant 1 and laden with fine coal and clay particles, comprising:

a) separating water from the particle laden wastewater in a thickener 2 to bring the particulate solids content thereof within the range of the order of 10 to of the order of 35 weight %, then,

b) mixing, in an agglomerating apparatus 4, the particle laden wastewater with oil agglomerating liquid, to micro-agglomerate fine, carbonaceous coal particles of the particle laden wastewater, the oil agglomerating liquid additive being added at not more than of the order of 20 weight % of the total weight of the solids of the particle laden wastewater,

c) separating the agglomerated fine, carbonaceous coal particles 6 from the remainder of the particle laden wastewater to leave particulate, inorganic material laden wastewater 8, and then,

d) dewatering the particulate, inorganic material laden wastewater by ultrafiltration, in an ultrafiltration apparatus 10, to leave a viscous, thickened particulate, inorganic material residue 12.

Depending on the characteristics of the inorganic material present in the wastewater 8, from the agglomerator 4, it may be desirable to use a thickener 14 after the agglomeration step by the agglomerator 4 and before the final ultrafiltration step by the ultrafiltration apparatus 10. Whether this is desirable or not for any particular wastewater laden with fine coal particles and clay can be determined by experiment.

The thickeners 2 and 14 may be any conventional thickener described, for example, in "Coal Preparation", K.K. Humphreys, W.F. Lawrence, B.G. McMillan and R.B. Muter, Fourth Edition, 1979, pages 12-33 to 12-54, published by the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc. The thickeners 2 and 14 may be, for example, any of those commonly known as "deep cone", "slope settler" or "filter".

Depending on the quality of the water needed from the thickeners 2 alone, or 2 and 14, water 20 and 22, respectively, from them may be filtered by ultrafiltration apparatus 16 and 18, respectively. This will be dictated by the particular use that is made of this water. This water may be recirculated to the coal preparation plant 1.

The agglomerating apparatus 4 may comprise three mixing devices having impeller blades for stirring the particle laden wastewater with the agglomerating liquid. One mixing device can be used provided that the residence time therein for micro-agglomeration of the carbonaceous coal particles is tolerable.

When three mixing devices are used, the first one is preferably a high shear mixing device, such as a conventional turbine mixer and is used to disperse the oil agglomerating liquid in the particle laden wastewater. The second and third mixing devices may be relatively lower blade speed, intermediate intensity mixing devices and are for producing

the micro-agglomerates. The preferred blade tip speed of the high shear impeller blades is in the range of the order of 10 m/sec to of the order of 30 m/sec, better still of the order of 25 m/sec. The preferred blade tip speed of the pitched, turbine impeller blades is up to of the order of 15 m/sec.

The preferred oil agglomerating liquids are No. 2 fuel oil and diesel oil. Other oils which may be used as the agglomerating liquid are, for example, light petroleum fractions, kerosene, coke oven light oil, and crude and residual and waste oils, and mixtures thereof. The quantity of oil agglomerating liquid used will depend upon the type of coal being processed and the particle size.

The agglomerates of fine, carbonaceous particles may be separated from the remainder on, for example, a sloping, stationary screen. However, they may be separated on, for example, by a sloping, vibrating screen, by an air flotation step, or by a wet cyclone separator if the micro-agglomerates possess sufficient strength not to be broken up in such apparatus.

Water 24 from the ultrafiltration apparatus may, for example, be recirculated to the coal preparation plant 1.

In Figure 2, similar parts to those shown in Figure 1, are designated by the same reference numerals and the previous description is relied upon to describe them.

In Figure 2, water is separated from the particle laden wastewater by ultrafiltration apparatus 24. The water 28 from the ultrafiltration apparatus may be recirculated to the coal preparation plant.

The following tests were made to verify that ultrafiltration apparatus 10 and 26 could be used in the manner described.

ULTRAFILTRATION MEMBRANES

Three sets of integrally supported tubular ultrafiltration membranes were used in these tests. Membranes in the first set were made

of cellulose acetate material, and those in the second and third sets were made of polysulfone materials. The cellulose acetate membranes were obtained from Electrohome Ltd., Montreal, Canada, and they were made by the differential gelation technique using the apparatus described in United States Patent 4,177,031, dated December 4, 1979, "Apparatus for Casting Tubular Polymeric Membranes For Reverse Osmosis and Ultrafiltration" by W.L. Thayer et al. The support tubes used for both kinds of membranes were porous (10 micron voids), high density polyethylene tubes of 3.81 cm (1½ inches) outside diameter, 0.635 cm (¼ inch) wall thickness, and 1.22 m (4 ft) length. The composition of the film casting solution and the other film casting conditions used for the cellulose acetate membranes were as follows:

Casting solution composition (wt %)

cellulose acetate (Eastman 400-25)	14.8
acetone	63.0
water	19.9
magnesium perchlorate	2.3
temperature of casting solution	22-25°C
solvent evaporation period	5s

gelation medium: ethyl alcohol-water as indicated below

module	inside gelation medium		outside gelation medium	
	wt% alcohol	temp	wt% alcohol	temp
1	45	20°C	95	30°C
2	40	20°C	95	30°C
3	35	20°C	95	30°C
4	30	20°C	50	20°C

gelation time	15 min
solvent leaching medium:	ice-cold water (1°C)
solvent leaching time	1 hr.

The initial data on pure water (distilled water) permeation rates (PWP) obtained with the above cellulose acetate membranes are given in Figure 3.

The membranes in the second and third sets were made of polysulfone [Udel - Union Carbide trademark] and polyethersulfone [Victrex - I.C.I. trademark] materials, respectively. The casting solution compositions (wt %) for these sets of membranes were as follows:

	Set 2	Set 3
Polymer	18	28
Additive	8[a]	5.6[b]
N-Methylpyrrolidinone	74	66.4

([a] polyethylene glycol-6000; [b] polyvinylpyrrolidone-10000).

MODULES

The modules used in this work were three-tube ultrafiltration modules. The effective membrane area in each module was 0.307 m^2 (3.3 ft^2). In most of the experiments, four modules were used in series. The feed flow was in parallel in the membrane tubes within each module, and was in series from module to module.

FEED CHARACTERISTICS

Two kinds of feed slurries used were: (a) pulverised coal in water, and (b) wastewater with suspended clay and other inorganic ash-forming particles from coal tailings. The source of coal used in feed (a) above was the Minto mines in New Brunswick, Canada; some of the properties (in wt %, dry basis) of this coal were typically as follows:

ash	20.7
total sulfur	8.3
inorganic (sulfate) sulfur	0.3
pyritic sulfur	6.5
organic sulfur	1.5

Particle size distribution (wt basis by Coulter Counter, Model TA II).

		Initial		After 75 hours in the operating circuit
10%	>	26.0 μm	>	25.0 μm
20%	>	18.1 μm	>	17.5 μm
30%	>	14.1 μm	>	13.5 μm
40%	>	11.1 μm	>	10.8 μm
50%	>	9.1 μm	>	8.8 μm
60%	>	7.4 μm	>	7.1 μm
70%	>	5.9 μm	>	5.7 μm
80%	>	4.5 μm	>	4.4 μm
90%	>	3.2 μm	>	3.1 μm
98%	>	1.7 μm	>	1.6 μm

The pH of the coal feed slurry was ∿3.0. Increasing the pH to > 7 caused precipitation of insoluble iron, and all of the tests were carried out without increasing the original pH of the coal-water feed.

The coal tailings used in feed (b) were those obtained in a pilot plant for spherical agglomeration using Valley Camp coal from Pennsylvania. The ash content of the coal tailings was 90% and the particle size distribution (wt basis) was as follows:

10%	>	22.5 μm
20%	>	14.0 μm
30%	>	9.8 μm
40%	>	7.4 μm
50%	>	5.6 μm
60%	>	4.5 μm
70%	>	3.2 μm
80%	>	2.2 μm
90%	>	1.4 μm
98%	>	0.6 μm

The pH of the clay-water feed slurry was < 6.0 in all the tests.

EXPERIMENTAL APPARATUS

The general flow diagram of the experimental apparatus used in the tests is shown in Figure 4.

In Figure 4 there is shown a feed tank 28, having a stirrer 30, a pump 32, a heat exchanger 34, a temperature sensor 36, a flow measuring

device 38, ultrafiltration modules 40 with flow meter 42 on the liquid inlet, flow meter 44 on the permeate outlet, flow meter 46 on the filtrate outlet, a recirculation pump 48, and a pressure control valve 50. The pump 32 was a Gould's multistage impeller pressure pump capable of pumping the feed slurry from atmospheric pressure to 2760 kPag (400 psig) at a flow rate of 5.678×10^{-2} m^3/min (15 gal/min). The pump 48 was a Worthington variable speed centrifugal booster pump capable of circulating the feed in the ultrafiltration loop at the selected operating pressure with rates in the range 7.57×10^{-2} to 34.1×10^{-2} m^3/min (20 to 90 gal/min) as desired. Thus the pump 32 and the pressure control valve 50 provided the pressure needed for the feed, and the recirculating pump 48 provided the flow rate needed for the feed in the ultrafiltration modules 40. The feed tank 28 was made of polyethylene, with a capacity of 0.473 m^3 (125 gallons). The tank 28 was provided with the stirrer 30 which prevented settling of solids in the tank.

During operation, the slurry from the feed tank 28 was pressurized by pump 32, and passed through the heat exchanger 34, which kept the temperature of the feed essentially constant at 25°C. The feed then entered the ultrafiltration modules 40. The concentrate from the modules 40 was returned to the feed tank 28, and the permeate from the modules was either returned to the feed tank 28 or routed to drains as desired. The operating pressure in the membrane tubes was kept in the range 69 to 690 kPag (10 to 100 psig). The membrane permeated product was always clear water, as confirmed by turbidity measurements, so that solids separation was essentially 100% in all runs. Both the feed flow rates and membrane permeated product-rates were measured by the flow meters 42, 44 and 46.

TEST RESULTS

Water Quality. Using an HF Turbidimeter [trademark] (Model DRT-100), data on turbidity of distilled water, tap water (available in

the laboratory), and permeate water obtained in the ultrafiltration (UF) runs were determined in Formazin Turbidity Units (FTU), and the quality of water was expressed as equivalent concentration of SiO_2 in the water on the basis that 10 ppm of SiO_2 is equivalent to 3 FTU. The results obtained were as follows:

Water	Turbidity Reading FTU	Equivalent Conc. SiO_2
Distilled water	0.10	0.33 ppm
Tap water	0.44	1.5 ppm
UF permeate water	0.30	1.0 ppm
Standard (provided by HF Instruments)	0.12	0.4 ppm

The above results show that the quality of UF permeate water was better than the tap water used in making up the feed slurries used in the ultrafiltration experiments. The results also show that the tap water used in this work contained enough suspended particulate and/or colloidal matter to give a turbidity reading more than 4 times that of distilled water.

Data on Pure Water Permeation (PWP) of Membranes After Coal-Water and Clay-Water Runs. The membrane modules were subjected to many coal-water and clay-water ultrafiltration runs during normal working hours for several months, and after all the above runs were completed, a set of PWP data on membranes was obtained using tap water feed. The results showed that at 276 kPag (40 psig) and a feed flow rate of 34.1×10^{-2} m^3/min (90 gal/min) per module, the PWP data were 8.28, 6.80, 5.90, and 4.45 $m^3/d\ m^2$ (212, 174, 151 and 114 gal/day ft^2) for modules 1, 2, 3 and 4, respectively. The above data may be compared with the initial PWP data of 100, 44.5, 19.9 and 5.47 $m^3/d\ m^2$ (2560, 1140, 510 and 140 gal/day ft^2) given in Figure 3. The results show that the drop in PWP from the original value is highest for the most porous membrane and is lowest for the least porous membrane. It is reasonable

to attribute the above drop in PWP partly to membrane compaction and mostly to partial blocking of membrane pores by the colloidal size particulate matter in the coal- and clay-water feeds. Even with such compaction and pore blocking, the final PWP data are high enough to be of practical interest for industrial ultrafiltration operations.

TESTS WITH COAL-WATER FEEDS

Effect of Operating Pressure and Feed Flow Rates

Using 2% coal-water slurry as the feed, several experiments were conducted in the operating pressure range 69 to 414 kPag (10 to 60 psig) at two feed flow rates, namely 17.0×10^{-2} and 34.1×10^{-2} m^3/min (45 and 90 gal/min) in each module (the feed flow rate through each membrane tube was one-third of that in the module). The results obtained are given in Figure 5. In each test, the water flux through the membrane usually dropped from an initial higher value to a steady state lower value within about one to three hours of continuous operation. Each data point in Figure 5 was obtained after at least 6 hours of continuous operation for the indicated operating pressure and feed flow rate. Therefore, the data given in Figure 5 may be considered as steady state values for the specified operating conditions.

Comparing generally the water flux data obtained in each module with the initial PWP data for the modules given in Figure 3, it is clear that the effects of membrane compaction due to operating pressure and pore blocking by colloidal size particulate matter in the feed are highest for the most porous membranes (module 1) and lowest for the least porous membranes (module 4); the corresponding effects on the membranes of intermediate porosity (modules 2 and 3) were sequentially intermediate between those obtained for the membranes in modules 1 and 4. These results show that the higher the porosity of the membrane, the higher is its susceptibility both for pressure compaction and colloidal pore blocking.

The data given in Figure 5 also show that feed flow rate had a significant effect on water flux through the membrane. Increase in feed flow rate from 17.0 m^3/min (45 gal/min) to 34.1 m^3/min (90 gal/min) in the module increased the water flux through the membrane from 22 to 25% in module 1, 27 to 36% in modules 2 and 3, and 23 to 51% in module 4 in the operating pressure range 138 to 414 kPag (20 to 60 psig). Such increased productivity at higher feed flow rate may be attributed to reduced solids build-up at the membrane-slurry interface, and hence reduced colloidal pore blocking, during ultrafiltration. The highest values for the water flux data obtained were 6.33, 5.47, 5.39, and 5.55 $m^3/d\ m^2$ (162, 140, 138, and 142 gal/day ft^2) for the membranes in modules 1, 2, 3, and 4 at the operating pressure of 138.0, 345, 414, and 414 kPag (20, 50, 60 and 60 psig), respectively. It may be noted that all the water flux data given above are attractive for possible industrial application. However, for such application, the membrane in module 1, which gave the highest water flux at the lowest operating pressure may not necessarily be the best one for practical use involving continuous operation for long periods, in view of the relatively greater susceptibility of the membrane for both pressure compaction and colloidal pore blocking. A membrane with a smaller average size of pore on the membrane surface may prove to be better for such long term continuous service provided it is economically acceptable to use a higher operating pressure to give the required water flux. From such consideraitons, the membranes used in each of the four modules studied in this work should be of practical interest in terms of industrial process optimization.

Figure 5 also shows that the water flux for the membranes in module 1 passed through a maximum flux which occurred at about 138 kPag (20 psig) for both the feed flow rates of 34.1×10^{-2} and $17 \times 10^{-2} m^3$/min (90 and 45 gal/min). The water flux data for the membranes in the other modules studied also exhibited similar tendencies to pass through maxima

with increase in operating pressure; further, the pressure at which the maximum flux occurred seemed to shift to a higher value as the average pore size on the membrane surface decreased. The existence of maxima in flux is due to the competing effects of the tendency for the water flux to increase with operating pressure and to decrease with increase in the extent of pore blocking and membrane compaction due to increase in the concentration of coal at the membrane-slurry boundary layer during ultrafiltration. Thus, the magnitudes of the maxima in water flux through the membranes are essentially functions of the average pore size on the membrane surface and the boundary concentration of coal during ultrafiltration.

Effect of Concentration of Coal in Feed Slurry on Water Flux Through Membranes. Figure 6 gives the water flux data obtained with the membranes used in modules 1 to 4 during batchwise concentration of coal-water slurry from 2 wt% to 50 wt% coal in the feed; these tests were conducted at 276 kPag (40 psig) at the feed flow rate of 34.1×10^{-2} m^3/min (90 gal/min) in each module, i.e. 11.4×10^{-2} m^3/min (30 gal/min) in each membrane tube. In such a batchwise concentration process, the coal concentration in the feed changes continuously with time, which probably explains the differences in the water flux data from that given in Figure 5. Each data point in Figure 6 corresponded to the coal concentration in the feed leaving the respective module. Several aspects of Figure 6 are of industrial interest.

The results show that concentration of coal in the feed slurry by ultrafiltration up to 50 wt% is practically achievable using the kind of membranes and modules employed in these tests. The decrease in water flux as a function of coal concentration in the feed is particularly interesting. This decrease is primarily due to increase in boundary concentration of coal on the membrane surface and colloidal pore blocking. While water flux decreased steeply with increase in coal concentration

in modules 1 and 2, such decrease was far less steep in modules 3 and 4. This result is attributable to the variations in pore size distribution in the membranes used in the four modules tested. The surface pore structure of all the membranes used may be expected to have a larger number of relatively smaller pores and a smaller number of relatively larger pores all of which are capable of separating the coal particles essentially completely during ultrafiltration. The data on water flux given in Figure 6 indicate that the contribution of larger pores to total water flux (PWP) is relatively higher for the membranes used in modules 1 and 2 than for the membranes used in modules 3 and 4. Since larger pores are more susceptible to colloidal pore blocking, the membranes used in modules 1 and 2 are more susceptible to such pore blocking and the consequent flux decrease during ultrafiltration than are the membranes used in modules 3 and 4.

Figure 6 also shows that the membranes used in module 3 had the highest water flux for higher concentrations (8 wt%) of coal in the feed slurry in spite of their lower PWP compared to the membranes used in modules 1 and 2. For example, for the feed slurry containing 4.5 wt% coal, the data on water flux were 1.13, 1.76, 3.40, and 2.27 $m^3/d\ m^2$ (29, 45, 87 and 58 gal/day ft^2) for the modules 1, 2, 3, and 4, respectively; and, for the feed slurry containing 50 wt% coal, the data on water flux were 0.23, 2.1, and 1.29 $m^3/d\ m^2$ (6, 54 and 33 gal/day ft^2) for modules 1, 3 and 4, respectively. These data indicate that, from the practical point of view, the membranes used in module 3 are obviously preferable to the other membranes tested in this work for possible industrial use in the ultrafiltration treatment of coal-laden waters. This observation confirms the conclusion made earlier that a membrane which gives the highest PWP, even though it gives 100% separation for coal, is not necessarily the best one to use for water reclamation and fines recovery in coal preparation plants.

Tests with Clay-Water Feed Slurries. Figure 7 gives the water flux data obtained with the membranes used in modules 1 to 4 during batchwise concentration of clay-water slurry from 0.1 wt% to 40 wt% of clay in the feed; these experiments also were conducted at 276 kPag (40 psig) at the feed flow rate of 34.1×10^{-2} m^3/min (90 gal/min) in each module (i.e. 11.4×10^{-2} m^3/min [30 gal/min] in each membrane tube). As in Figure 6, each data point in Figure 7 corresponded to the clay concentration in the feed leaving the respective module.

In view of the identical operating conditions, the water flux data given in Figures 6 and 7 are directly comparable. Figure 7 shows that clay concentrations up to 40 wt% is practically operable using the kind of membranes and modules employed in this work. With clay-water feed slurries, the data on water flux obtained were relatively lower in all the four modules tested compared to the corresponding data obtained for the coal-water feed slurries. Further, the relative decrease in water flux as a function of clay concentration in the feed was similar for all the four modules in contrast to the corresponding data obtained for the coal-water slurries. These results indicate that the colloidal pore blocking effect is relatively more with the clay-water feed slurries, which is not surprising in view of the fact that the clay particles were relatively finer than the coal particles in the feed slurries used as shown by the data on particle size distribution given earlier. For the treatment of clay-water slurries, the membranes used in module 1 had the highest water flux for most of the range of clay concentrations studied. These results indicate the existence of unique combinations of pore size distribution on the membrane surface and particle size distribution in the feed slurry for optimum water flux through membranes for different feed constituents and membrane materials even under otherwise identical experimental operating conditions. Such combinations need further experimental exploration for quantitative identification.

Tests with Polysulfone Membranes. Figure 8 gives the water flux data obtained with the polysulfone membrane modules used during the batchwise concentration of coal-water slurry from 0.1% to > 20% (by weight) coal in the feed. These experiments were also conducted at 276 kPag (40 psig) at the feed flow rate of 34.1×10^{-2} m^3/min (90 gal/min) in each module. As before, each data point in Figure 8 corresponded to the coal concentration in the feed leaving the module. The results given in Figure 8 are comparable to those given in Figure 6 for the cellulose acetate membrane modules. For illustration, a set of comparative data is given in the following table.

Membrane module	Water flux ($m^3/d\ m^2$) at coal concentrations of 1%	10%	20%
CA-Module 3 (Fig.4)	7.75	7	6.8
PS-U-200 (Fig.6)	6.5	6.5	5
PS-V-3500 (Fig.6)	13	9.5	7.5

The above data show that the performance of polysulfone membrane modules were generally just as good or better than the cellulose acetate membrane modules in the range of solids (coal) concentration studied. With the available data, no decisive statement on the superiority of the polysulfone membrane modules is warranted; however, polysulfone membranes are preferred because of their resistance to abrasion, particularly in ultrafiltration apparatus 10 in Figures 1 and 2.

Processing Capacities of Membranes for Coal- or Clay-Fines Concentration. The processing capacity of a membrane may be defined as the weight W of initial feed slurry in kilograms that one square meter of film surface can handle per day in a batchwise concentration process to increase the solids concentration from the initial weight fraction Z_i to the final weight fraction Z_f. If q represents the water flux through the membrane (in kg/m^2 day) at any given solids concentration Z

(in wt fraction) in the feed slurry, then

$$W = [Z_i \int_{Z_f}^{Z_i} \frac{1}{q} d\left(\frac{1}{Z}\right)]^{-1} \qquad (1)$$

Equation 1 is derived in the publication "Reverse Osmosis" S. Sourirajan, Ch. 6, Academic, New York, 1970. Using the test results given in Figures 6, 7 and 8 and Eqn. 1, the processing capacities of some of the membranes used for the concentration of coal and clay fines studied in this work were calculated, and the results obtained are given in Figure 9. These results illustrate the practical industrial utility of the membranes and modules studied in this work.

The data from these tests confirm the potential applicability of cellulose acetate and polysulfone ultrafiltration membranes for water and coal recovery and reuse from wastewaters containing suspended coal and clay particles.

CLAIMS:

1. A method of treating wastewater laden with fine carbonaceous coal and inorganic particles, comprising:

(a) separating water from the particle laden wastewater to bring the particulate solids content thereof within the range of the order of 10 to of the order of 35 weight %, then

(b) mixing the particle laden wastewater with light oil agglomerating liquid having a specific gravity of less than of the order of 1 g/cm^3, to micro-agglomerate fine, carbonaceous coal particles of the particle laden wastewater, the light oil agglomerating liquid additive being added at not more than of the order of 20 weight % of the total weight of the solids of the particle laden wastewater,

(c) separating the agglomerated fine, carbonaceous coal particles from the remainder of the particle laden wastewater to leave particulate, inorganic material laden wastewater, and then

(d) dewatering the particulate, inorganic material laden wastewater by ultrafiltration to leave a viscous, thickened particulate, inorganic material residue.

2. A method according to claim 1 wherein the water is separated from the particle laden wastewater, to bring the particulate solids content within the range of the order of 10 to of the order of 35 weight %, by ultrafiltration.

3. A method according to claim 1 wherein the water is separated from the particle laden wastewater, to bring the particulate solids content within the range of the order of 10 to of the order of 35 weight %, by thickening the particle laden wastewater to clarify water thereof and then separating the clarified water therefrom.

4. A method according to claim 1 wherein water is separated from the particulate, inorganic material laden wastewater, from which the agglomerated carbonaceous particles have been removed, by thickening the particulate, inorganic laden wastewater, prior to the dewatering by ultrafiltration.

5. A method according to claim 1 wherein the dewatering of the particulate, inorganic material laden wastewater, brings the particulate solids content thereof to greater than of the order of 40 weight %.

6. A method according to claim 4 wherein water from the said thickening step is purified by ultrafiltration.

7. A method according to claim 1 wherein the ultrafiltration step is carried out using porous, polysulfone ultrafiltration membrane material.

8. A method according to claim 2 wherein the ultrafiltration step to separate water, to bring the particulate solids content within the range of the order of 10 to of the order of 35 weight %, is carried out using porous, polysulfone ultrafiltration membrane material.

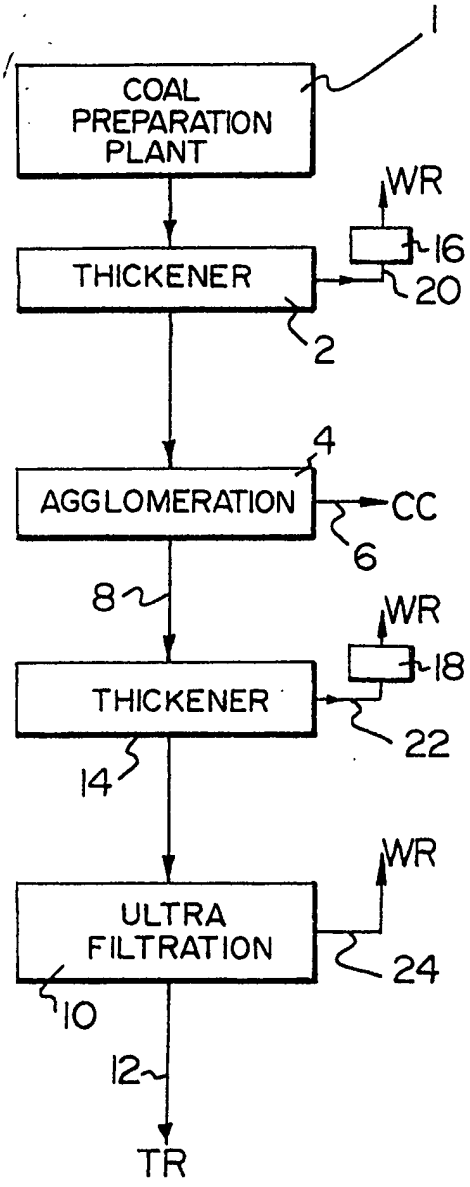

FIG. 1

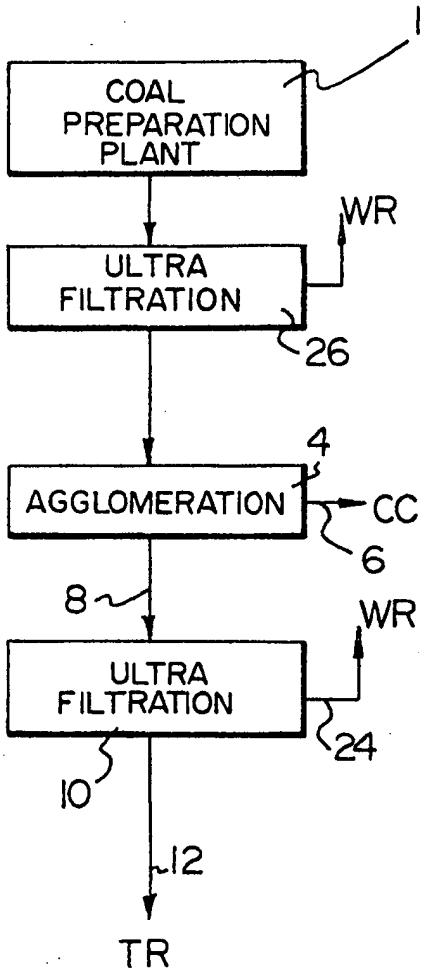

FIG. 2

Francis O'Connor
PATENT AGENT

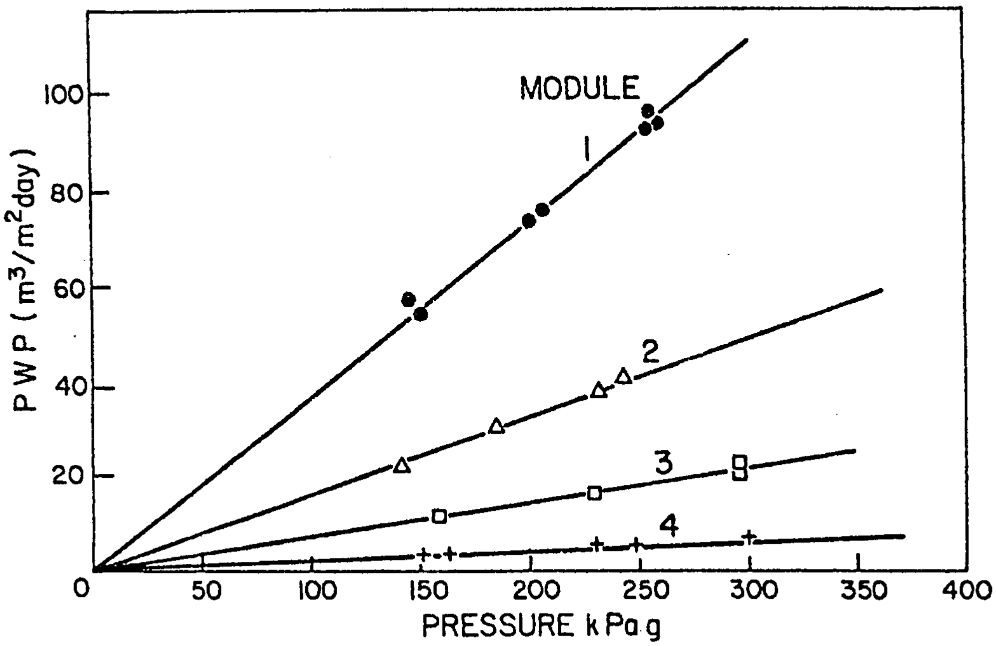

FIG. 3

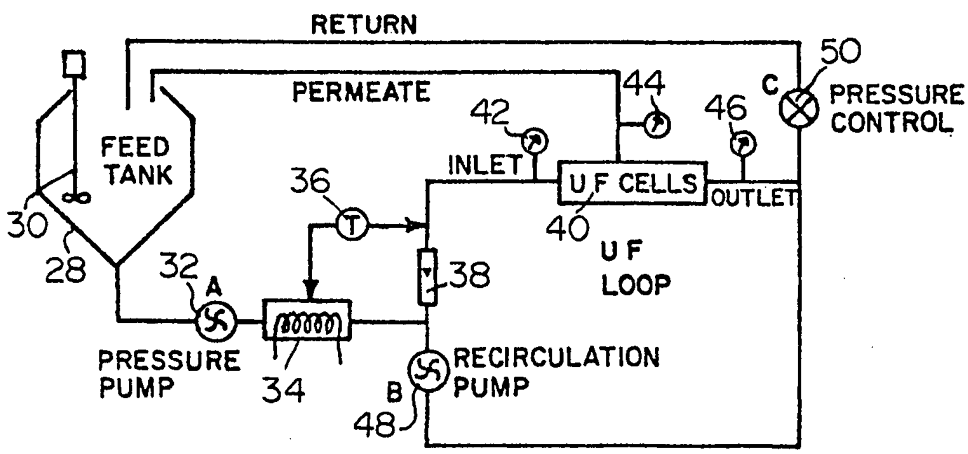

FIG. 4

Francisco Lemon

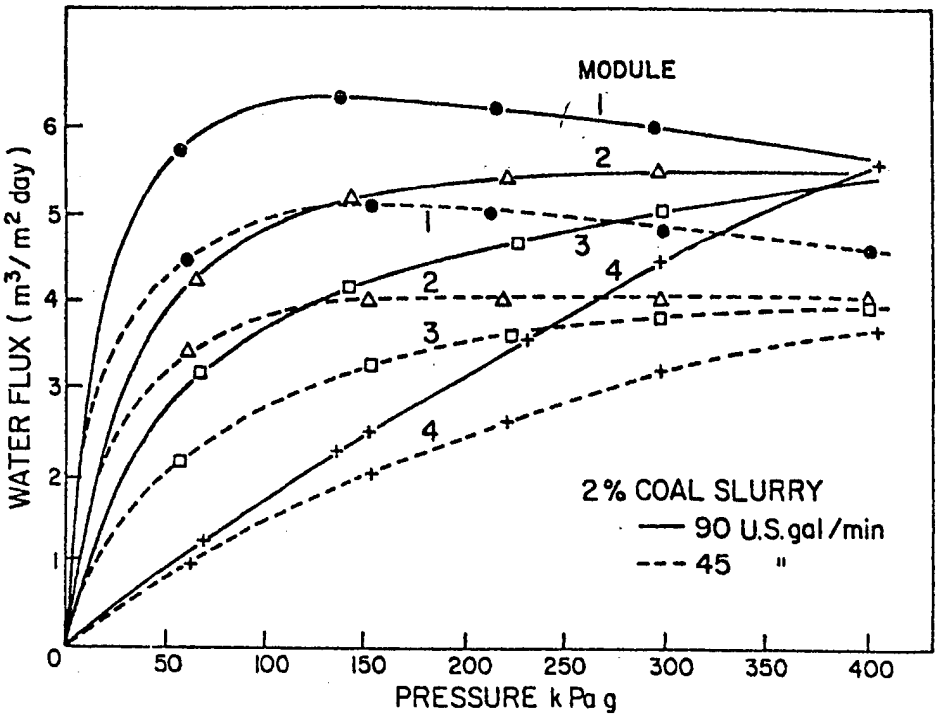
MODULE
1
2
3
4
2% COAL SLURRY
90 U.S.gal/min
45 "
WATER FLUX (m^3/m^2 day)
PRESSURE k Pa g
0
1
2
3
4
5
6
50
100
150
200
250
300
350
400

FIG. 5

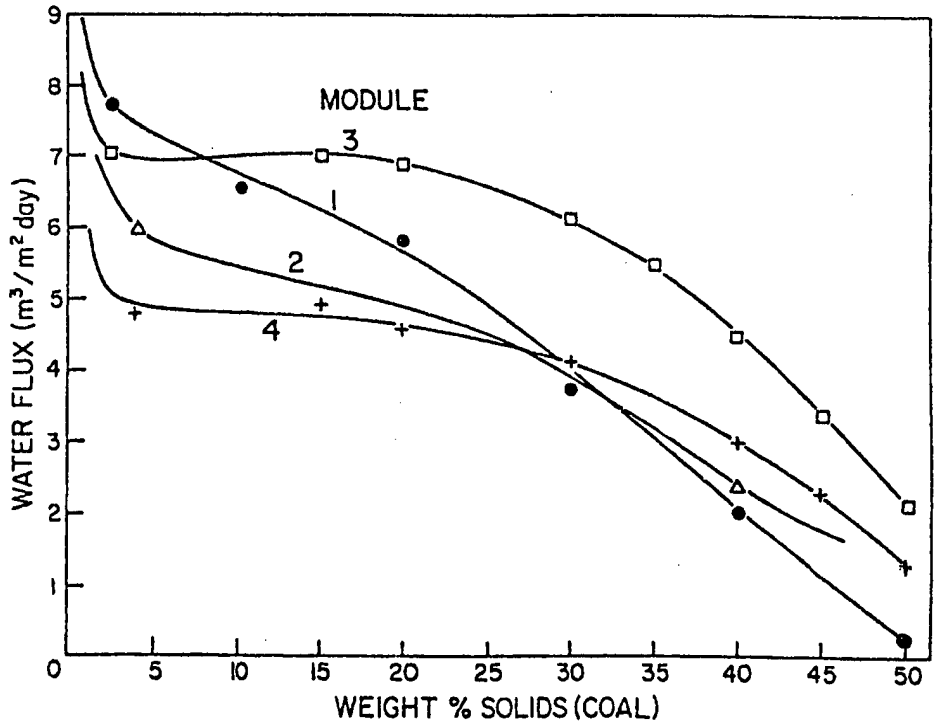
MODULE
1
2
3
4
WATER FLUX (m^3/m^2 day)
WEIGHT % SOLIDS (COAL)
0
1
2
3
4
5
6
7
8
9
5
10
15
20
25
30
35
40
45
50

FIG. 6

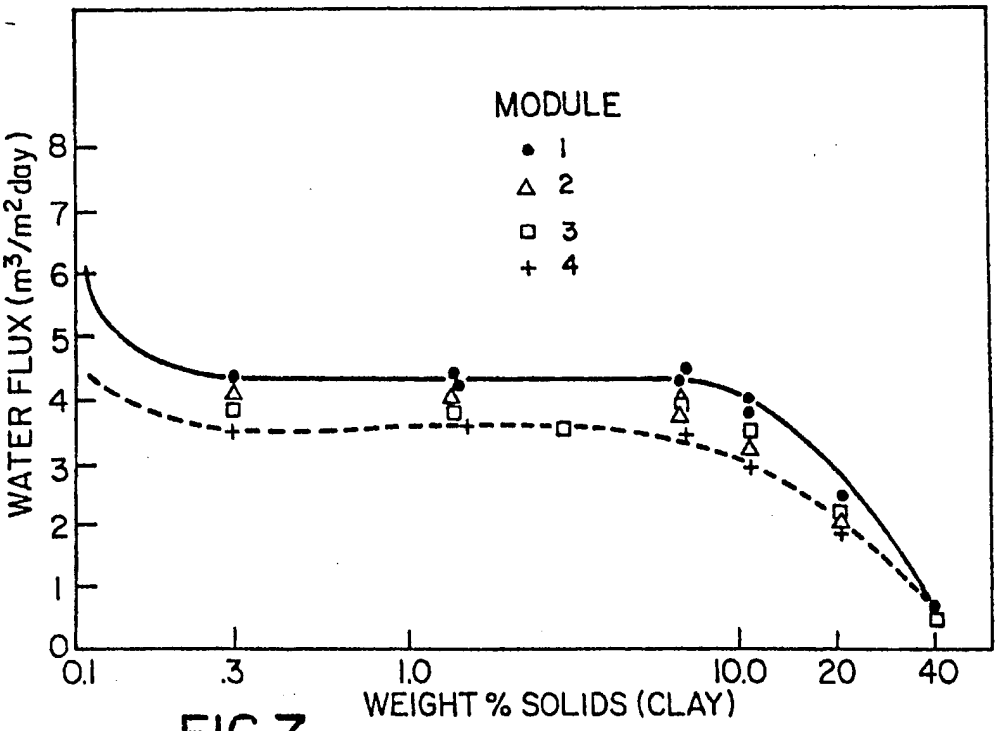

FIG.7

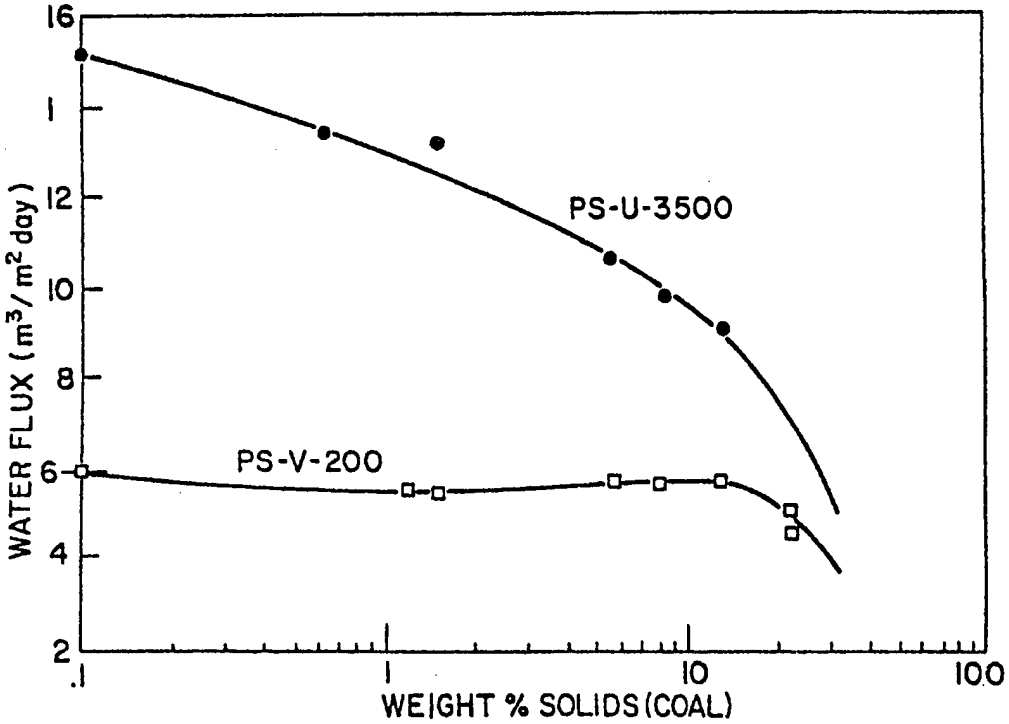

FIG.8

Francis W. Lemon

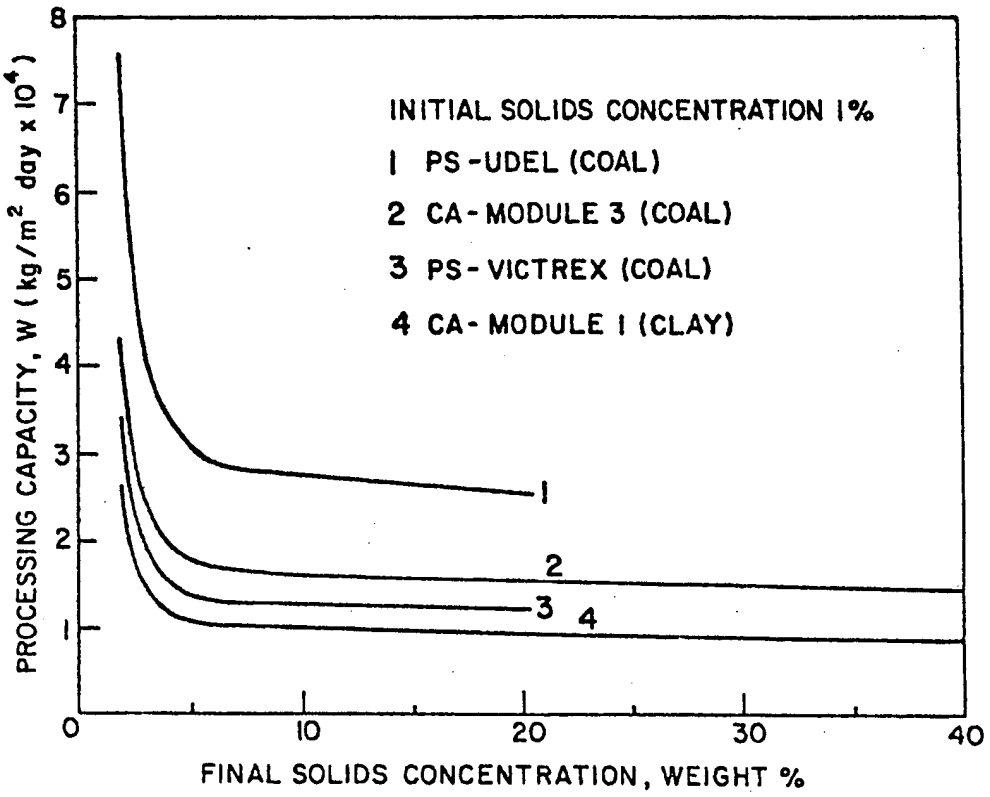

FIG. 9

Francis A Lemon